INTERSTRATIFICATION IN VERMICULITE

by

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ABSTRACT

VERMICULITE (Libby, Mont.) was ground in a Waring blender in a 1 M NaCl solution and, after removal of excess electrolyte, the clay fraction was separated by sedimentation. The clay was predominantly vermiculite: X-ray diffraction patterns of Ca-saturated and oriented specimens showed an intense and sharp 15 Å and a weak 25 Å diffraction maxima and their integral orders. The intensity of the 25 Å reflection, attributed to regularly interstratified layers of vermiculite (15 Å) and mica (10 Å), was less than 20% of the 15 Å peak.

Additions of varying amounts of potassium or cesium, ranging from 10% to 100% of exchange capacity, to Ca-saturated clay showed that the collapse of the vermiculite lattice proceeds through a 1:1 regular interstratification of a 15 Å and a 10 Å lattice. Successive additions increased the 25 Å diffraction peak at the expense of the 15 Å reflection until the entire sample was interstratified. Further additions of K (or Cs) reduced the intensity of the 25 Å reflection and produced a 10 Å reflection until the entire sample was collapsed to 10 Å and no 25 Å reflection was recorded. These observations point out that under certain environmental conditions, the diagenetic formation of micas from vermiculite may proceed through an interstratification of the two in a manner analogous to weathering of biotite to vermiculite through an interstratified stage.

One-dimensional Fourier synthesis from the intensities of the 00*l* diffraction maxima of the interstratified mixture was carried out. In addition, a mechanism for the formation of the interstratified mixture was postulated: the replacement of Ca by K (or Cs) in one layer reduces the effective negative charge on the adjacent layer. Consequently, the K cannot replace the Ca in this but replaces the Ca in the next layer forming the interstratified mixture.

INTRODUCTION

NUMEROUS examples of randomly interstratified layer silicates in mineral deposits and in soil clays have been reported. The occurrence of regularly interstratified layer silicates is scarce, however. Three well-known examples of alternating 10 Å (mica) and 14 Å (vermiculite) layers are hydrobiotite (Gruner, 1934), rectorite (Bradley, 1950), and allevardite (Caillère, Mathieu-Sicaud, and Hénin, 1950; Brindley, 1956). This report describes the formation in the laboratory of a regularly interstratified mica–vermiculite layer sequence.

The presence of biotite in the lower horizons of some soils, of interstratified biotite–vermiculite in the intermediate horizons, and of vermiculite in the

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upper horizons and in weathered biotite particles led to the postulate that biotite weathers to vermiculite through an intermediate interstratified stage (Walker, 1950; Jackson *et al.*, 1952; Stephen, 1952). Laboratory weathering of biotite by treatment with Mg salts also yielded vermiculite but no mixed layers were formed (Barshad, 1948). On the other hand, extraction of K with sodium tetraphenylboron produced randomly interstratified mixtures in certain instances (DeMumbrum, 1959) and vermiculite in others (Mortland, 1958; Scott and Reed, 1962). Also, the diffraction patterns of mica after treatment with 10^{-3} N $SrCl_2$ solution indicated the presence of a mixed layer phase with partial ordering (Rausell-Colom *et al.*, 1965). In addition to the several observations of the weathering of biotite either to randomly interstratified mixtures or to vermiculite, the formation of a regularly interstratified mixture from biotite has also been observed. Thus, on heating biotite in a 1 M $CuCl_2$ solution, Bassett (1958) obtained a regularly interstratified biotite–vermiculite mixture.

The reversion of vermiculite to mica-like materials has also been found to proceed through a randomly interstratified mixture under some conditions (Bassett, 1959) and directly to mica under others (Barshad, 1948). Recent experiments on the sorption of Cs from dilute solutions by vermiculite indicate that Cs may collapse the alternate layers of vermiculite (Sawhney, 1966) giving a regularly interstratified sequence. This investigation demonstrates the conversion of vermiculite to mica through a successive closure of the alternate vermiculite layers to form a regularly interstratified mica–vermiculite intermediate. The interstratified material is described and identified here.

EXPERIMENTAL

The vermiculite (Libby, Mont.) was obtained from Ward's Natural Science Establishment, Rochester, New York. A stock suspension of the clay was prepared as described previously (Sawhney, 1964). Briefly, the vermiculite was ground in a Waring blender in the presence of 1 M NaCl which was renewed several times. Excess electrolyte was then removed and the clay was separated by sedimentation. Grinding in the presence of NaCl yielded clay that contained mostly expanded vermiculite layers.

Increasing amounts of CsCl tagged with Cs-137 or KCl solution were added to aliquots of clay, and the suspensions were allowed to equilibrate. After several days, the suspensions were centrifuged. The colloid was resuspended in water, poured on a glass slide, and left to dry in air overnight. Then the lattice spacings of the oriented samples were measured with a Norelco wide-angle goniometer and a flat specimen holder. The supernatant solutions were analyzed for Cs, and some were also analyzed for K. Cesium was determined from the radioactivity of the solution, and K was determined with a flame photometer. Cesium or K sorbed by the clay was found from the difference in the concentration of these ions in the solution added and their concentration in the supernatant. Cation exchange capacity was determined by the

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method of Sawhney *et al.* (1959), and elemental analysis performed according to Jackson (1958). Intensities of the reflections on X-ray diffraction patterns were measured from the peak area, and the structure factors were calculated using a FORTRAN crystallographic least square program, OR FLS, obtained from the Oak Ridge National Laboratory through Dr. H. W. Wyckoff, Yale University, New Haven.

RESULTS AND DISCUSSION

Formation of Regularly Interstratified Mica–Vermiculite

The X-ray diffraction pattern of the Ca-saturated clay (curve 1, Fig. 1) shows a large and intense 15 Å and a small 25.2 Å diffraction maximum and their higher integral order reflections. Thus, the clay consists primarily of the expanded 15 Å layers attributed to vermiculite; only a small proportion of the clay is an interstratified mixture of 10 Å (mica) and 15 Å (vermiculite) layers giving a 25.2 Å reflection.

The X-ray analysis of Ca-vermiculite to which varying amounts of Cs ranging from 10% to 100% of its CEC were added showed that the collapse of the vermiculite lattice to mica lattice proceeds through a regular interstratification of a 15 Å and a 10 Å layer: diffraction patterns of the Ca-vermiculite after sorption of Cs equivalent to about 15% and 29% of its CEC (curves 2, 3) show that as the clay sorbed more Cs, the interstratified component with a 25.2 Å spacing giving integral higher order reflections increased while the expanded vermiculite with a 15 Å spacing decreased. When as much as 41% of the exchange sites were occupied by Cs, most of the vermiculite was converted into a 1:1 regularly interstratified mica–vermiculite layer sequence (curve 4). A slight hump towards the 15 Å reflection indicates that a small portion of the clay still remains as a separate expanded phase.

Additions of Cs to the interstratified mixture then collapsed the expanded layers within the mixture, producing a separate 10.8 Å phase and a concomitant reduction in the 25.2 Å phase. Thus, when about 60% of the exchange sites were occupied by Cs, a distinct 10.8 Å reflection appeared, and the intensity of the 25.2 Å reflection was reduced (curve 5). Further additions of Cs collapsed more layers to 10.8 Å and reduced the 25.2 Å layers still further until all the layers were collapsed and only a 10.8 Å and its higher order reflections were recorded (curve 6).

Since K is also known to collapse the expanded lattice of 2:1 layer silicates to a 10 Å lattice, the effect of K on the expanded lattice of vermiculite was determined by the same procedure as used for the collapse by Cs. Potassium affected the closure of the vermiculite layers in the same way as Cs. Successively larger additions of K collapsed more alternate layers, thus increasing the regularly interstratified 25.2 Å component and decreasing the 15 Å component (curves 2, 3, Fig. 2) until much of the sample was interstratified (curve 4) and finally the 15 Å spacing disappeared (curve 5). Further additions collapsed the expanded layers within the interstratified phase resulting in a

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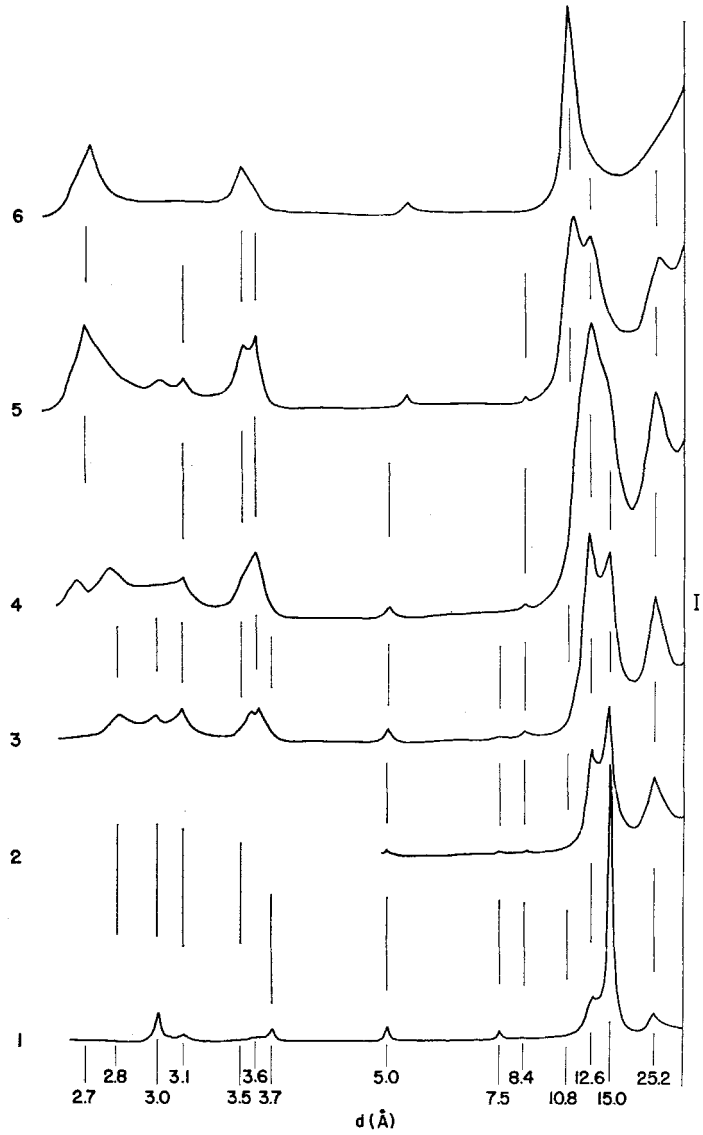


FIG. 1. Smoothed traces of X-ray diffraction patterns of Ca-saturated vermiculite (1) to which successively larger amounts of CsCl were added (2, 3, 4, 5, 6); showing the closure of vermiculite to mica through the collapse of alternate layers.

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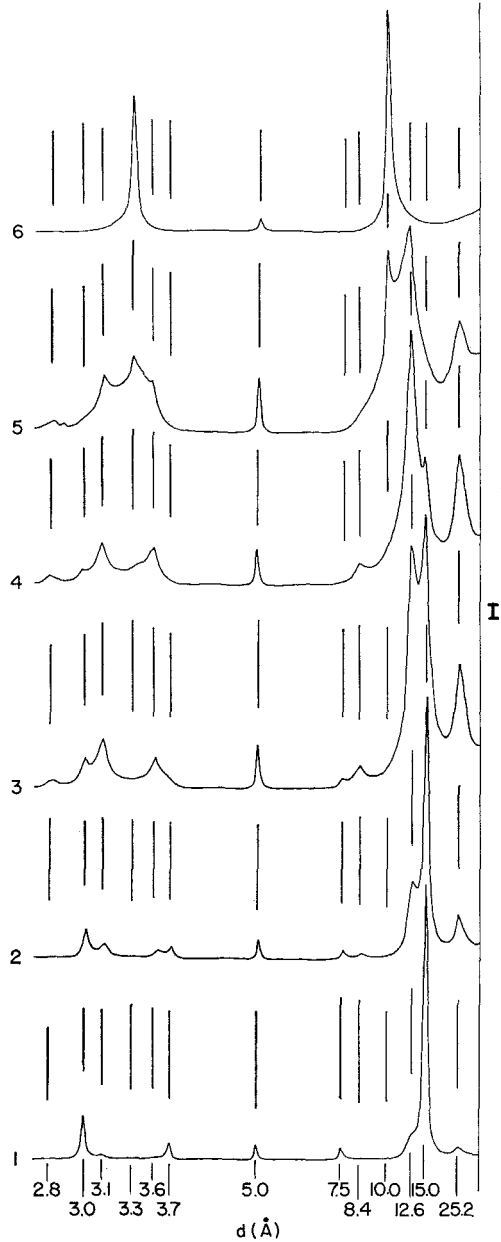


FIG. 2. Smoothed traces of X-ray diffraction patterns of Ca-saturated vermiculite (1) to which successively larger amounts of KCl were added (2, 3, 4, 5, 6); showing the closure of vermiculite to mica through the collapse of alternate layers.

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separate 10 Å reflection (curve 5), and finally (curve 6) only a 10 Å reflection and its orders could be seen.

Chemical Analysis and Structural Formula of Vermiculite

The clay fraction of Libby vermiculite was analyzed, and the major oxides are listed in Table 1. Because the clay was saturated with Na prior to chemical analysis, Na_2O was assumed to be equal to the CEC (140 me per 100 g) of the clay. Iron was determined as the Fe^{3+} ion. Potassium was assumed to be the interlayer cation of the biotite component present as the interstratified mixture in the clay and hence does not appear in the structural formula. Further, apart from the interlayer cation, the chemical composition of biotite was assumed to be the same as vermiculite in the clay. The chemical composition of a coarser fraction of vermiculite from Libby (Schnepfe, 1960) showed only slightly less Si and Al and slightly more Mg. The structural formula (Table 1) determined from these analyses was used later in the structure factor calculations, except for the cationic composition of the interlayers. The structure factors given in Table 2 were calculated on the assumption that in the interstratified mixture, Ca and K occupied the alternate layers.

TABLE 1.—CHEMICAL COMPOSITION AND FORMULA FOR LIBBY VERMICULITE

Oxide	%
SiO_2	37.87
Al_2O_3	13.13
MgO	16.40
Fe_2O_3	10.38
K_2O	2.13
Na_2O	4.34
H_2O	15.20

Structural formula: $(Si_{2.97}Al_{1.03})\ (Mg_{1.92}Fe_{0.58}Al_{0.19})\ O_{10}(OH)_2 \cdot 0.66\ Na$, where Na represents the exchange charge.

Fourier Analysis of Interstratified Mixture

Relative intensities of ten orders of the 25.2 Å 001 reflection were converted to relative structure factors by correcting them for Lorentz and polarization effects. The relative intensities of different orders of reflections from the interstratified component in several samples were similar. However, since curve 4 (Fig. 2) represented the most completely interstratified sample and showed the least of other phases, the relative intensities from this pattern were converted to structure factors (Table 2). Because the basally oriented

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samples are similar to single crystals, the correction for single crystals was used:

$$F^2_{00l} \propto I_{00l} \frac{\sin 2\theta_{00l}}{1+\cos^2 2\theta_{00l}} \quad [1]$$

F_{00l} is the observed relative structure factor for the lth order; I_{00l} is the intensity of the $00l$ reflections and θ is the angle of reflection.

The calculated structure factors were obtained from the chemical formula in Table 1 and the equation

$$F_{00l} = \sum_{m=1}^{N/2} f_n \cos 2\pi l z_m \quad [2]$$

where F_{00l} is the calculated structure factor for the lth order; f_n is the ionic scattering factor of the nth element in the structure and lz_m is the fractional measure of the intercept of the nth element on the c-axis. The summation was carried out over half the unit cell as the projection of the unit cell upon the c-axis has a center of symmetry at $Z=c/2$. The distances between the various sheets of ions within the structure were assumed to be the same as used for allevardite by Brindley (1956) with one exception: because Ca was the only interlayer cation in the expanded layers, the interlayer distance of the expanding layers here was assumed slightly larger.

TABLE 2.—X-RAY DATA FOR INTERSTRATIFIED MIXTURE

l	d_{00l} (Å)	$\lvert F\rvert_{obs}$	F_{calc}
1	25.20	93.6	93.6
2	12.60	147.9	−72.5
3	8.40	30.2	2.6
4	6.30	tr	10.7
5	5.04	59.2	−57.1
6	4.20	tr	−4.2
7	3.60	48.9	−9.6
8	3.15	118.9	−105.0
9	2.80	31.4	−11.8
10	2.50	46.9	25.2

Whereas the observed and the calculated structure factors (Table 2) for some reflections are in good agreement, for others they are not. Agreement between the observed and the calculated structure factors is especially good for the reflections from the first, fifth and eighth orders. The reflections from 10 Å or 15 Å component do not interfere with these orders since no reflection corresponding to the first and eighth order occurs from the 10 Å or 15 Å component. Further, their contribution to the fifth order of 25.2 Å is small. The lack of agreement is most pronounced for reflections that are common to the 10 Å and 15 Å phases also. Reflections from 15 Å or 10 Å phases were present in all X-ray patterns of the samples containing a 25.2 Å phase. Because the coexistence of the second order of the 25.2 Å reflection and the first order of the 10 Å and 15 Å confuse a quantitative estimate of the intensity of the

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individual reflections, the discrepancy between the observed and the calculated factors of l of 2 and of reflections common with other orders of 10 Å and 15 Å reflections is attributed to these interferences.

The agreement between the observed and the calculated structure factors from Fourier analysis of several reflections from the 25.2 Å phase verifies the collapse of the alternate layers with the formation of a regularly interstratified mica–vermiculite intermediate.

Mechanism of Regular Interstratification

To explain the formation of hydrobiotite from biotite, Bassett (1958) suggested that when K in one layer of biotite is replaced by hydrated Ca or Mg the bonding of that layer decreases while the bonding in the adjacent layer increases. Therefore, the next layer of K ions to be replaced by the hydrated ions is not the adjacent layer, since that is now more tightly bound, but the layer beyond the adjacent layer. However, Bassett did not explain how K in the layer adjacent to that occupied by the hydrated ion is more strongly held than before.

The present formation of a hydrobiotite-like material from vermiculite should be the reverse of the formation of hydrobiotite from biotite. Consequently, the following mechanism is proposed to explain the collapse of the alternate layers of vermiculite and the formation of regularly interstratified mica–vermiculite layers: The collapse of the alternate layers in the Ca-saturated vermiculite by K or Cs requires that the collapse of one layer must affect the adjacent layer, preventing replacement of the hydrated cation by K or Cs in this layer. The replacement of Ca and the two layers of water molecules surrounding the Ca ion decreases the distance between the K ion and the negatively charged silica sheet 1. Consequently, the distance between the center of the interlayer cation and the surface of the silicate sheet 2 is reduced from 9.35 Å when hydrated Ca is the interlayer cation to 8.02 Å when K is the interlayer cation (Fig. 3). Because the replacement of Ca by K or Cs also removes the two layers of water molecules, the dielectric constant of the interlamellar region decreases from about 80 for water to about 6 for mica. As a result of the decrease in the distance and the removal of interlayer water, more than five-fold increase occurs in the electrostatic force between a unit positive charge on the cation and a unit negative charge on the silicate sheet 2. This increased force effectively reduces the negative charge on silicate sheet 2. It must be assumed, then, that the bonding energy of K to silicate sheet 2 of reduced effective charge is smaller than the hydration energy of the Ca ions. Therefore, K would not enter the layer adjoining the sheet 2 but would enter the next layer, resulting in the formation of a regularly interstratified layer sequence. A similar mechanism may operate in the formation of a regularly interstratified 20 Å phase where Mg-vermiculite is dehydrated (Walker, 1956); dehydration of one layer may affect the next layer as the collapse of one layer by K or Cs in the present investigation.

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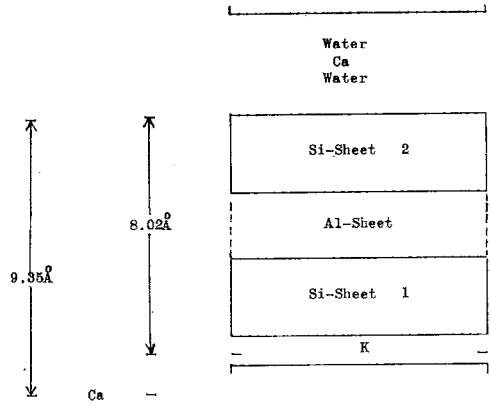


FIG. 3. Diagrammatic representation of the collapse of alternate vermiculite layers on replacing interlayer Ca and water by K.

CONCLUSIONS

Successively increasing additions of K or Cs to an expanded lattice of vermiculite containing a hydrated interlayer cation, Ca, first collapsed alternate layers of vermiculite resulting in the formation of a regularly interstratified 25.2 Å mica–vermiculite intermediate. The regularly interstratified layer sequence was verified by a one-dimensional Fourier analysis. Further additions of K or Cs collapsed the expanded layers within the interstratified mixture until the entire mixture was collapsed to a 10 Å mica lattice.

A mechanism was postulated to explain the collapse of alternate layers: the replacement of interlayer Ca and water by K or Cs in one layer reduces the effective negative charge on the adjacent layer. Consequently, the bonding energy between the K ion and the silicate sheet of reduced charge must become smaller than the hydration energy of the Ca ion. Hence, K cannot replace the hydrated Ca in this layer but replaces the Ca in the next layer. Thus, the sorption of K collapses the alternate layers resulting in a regularly interstratified mica–vermiculite.

The collapse of the alternate layers of vermiculite as increasing amounts of K were added shows that under certain environmental conditions, the diagenetic formation of illitic materials (Weaver, 1958) from the expanded layer silicates may proceed through a regularly interstratified layer sequence as in this study.

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REFERENCES

BARSHAD, I. (1948) Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curves, and water content: *Amer. Min.* **33**, 655–78.

BASSETT, W. A. (1958) Copper vermiculites from Northern Rhodesia: *Amer. Min.* **43**, 1112–33.

BASSETT, W. A. (1959) The origin of vermiculite deposit at Libby, Montana: *Amer. Min.* **44**, 282–99.

BRADLEY, W. F. (1950) The alternating layer sequence of rectorite: *Amer. Min.* **35**, 590–5.

BRINDLEY, G. W. (1956) Allevardite, a swelling double-layer mica mineral: *Amer. Min.* **41**, 91–103.

CAILLÈRE, S., MATHIEU-SICAUD, A., and HÉNIN, S. (1950) Nouvel essai d'identification du minéral de la table près Allevard, l'Allevardite: *Bull. Soc. Franç. Min. Crist.* **73**, 193–201.

DEMUMBRUM, L. E. (1959) Exchangeable potassium levels in vermiculite and K-depleted micas, and implications relative to potassium levels in soils: *Soil Sci. Soc. Amer. Proc.* **23**, 192–4.

GRUNER, J. W. (1934) The structures of vermiculites and their collapse by dehydration. *Amer. Min.* **19**, 557–75.

JACKSON, M. L. (1958) Elemental analysis of mineral colloids, soils, minerals and rocks: *Soil Chemical Analysis*, Ch. 11, pp. 278–300. Prentice-Hall, Inc., Englewood Cliffs, N.J.

JACKSON, M. L., HSEUNG, Y., COREY, R. B., EVANS, E. J., and VANDEN HEUVEL, R. C. (1952) Weathering sequence of clay size minerals in soils and sediments, II. Chemical weathering of layer silicates: *Soil Sci. Soc. Amer. Proc.* **16**, 3–6.

MORTLAND, M. M. (1958) Kinetics of potassium release from biotite: *Soil Sci. Soc. Amer. Proc.* **22**, 503–8.

RAUSELL-COLOM, J. A., SWEATMAN, T. R., WELLS, C. B., and NORRISH, K. (1965) Studies in the artificial weathering of mica: *Experimental Pedology* (edited by E. G. HALLSWORTH and D. V. CRAWFORD), Ch. 1, pp. 40–72, Butterworths, London.

SAWHNEY, B. L., (1964) Sorption and fixation of microquantities of cesium by clay minerals, effect of saturating cations: *Soil Sci. Soc. Amer. Proc.* **28**, 183–6.

SAWHNEY, B. L. (1966) Kinetics of cesium sorption by clay minerals: *Soil Sci. Soc. Amer. Proc.* **30**, 565–9.

SAWHNEY, B. L., JACKSON, M. L., and COREY, R. B. (1959) Cation-exchange capacity determination of soils as influenced by the cation species: *Soil Sci.* **87**, 243–8.

SCHNEPFE, M. M. (1960) Cation exchange with vermiculite: in *Short Papers in the Geological Sciences*, U.S. Geol. Survey Prof. Paper **400B**, Art. 71, p. B162.

SCOTT, A. D., and REED, M. G. (1962) Chemical extraction of potassium from soils and micaceous minerals with solutions containing sodium tetraphenylboron, II. Biotite: *Soil Sci. Soc. Amer. Proc.* **26**, 41–5.

STEPHEN, I. (1952) A study of rock weathering with reference to the soils of the Malvern Hills. Part I. Weathering of biotite and granite: *J. Soil Sci.* **3**, 20–33.

WALKER, G. F. (1950) Trioctahedral minerals in the soil clays of northeast Scotland: *Mineralog. Mag.* **29**, 72–84.

WALKER, G. F. (1956) The mechanism of dehydration of Mg-vermiculite: *Clays and Clay Minerals*, Proc. 4th Conf., Natl. Acad. Sci—Natl. Res. Council, Pub. 456, 101–15.

WEAVER, C. E. (1958) The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite and volcanic material: *Amer. Min.* **43**, 839–61.

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